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ORIGINAL PAPER

Enhanced CO_2 Methanation by New Microstructured Reactor Concept and Design

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Abstract

A novel multichannel minireactor with channel internal diameter in the range of millimeters has been conceptually designed and constructed. Its configuration confers to the new concept reactor some features and advantages compared to conventional fixed-bed reactors g.e. better mass-transfer, avoid hot-spots formation, increased performance (10–20%). Consequently, this new reactor concept is ideal to be applied to exothermic reactions such as the Sabatier reaction that demands continuous removal of the heat produced to avoid hot-spot formation and the sintering of the catalyst. Thanks to its configuration, this reactor could control effectively the heat generated by the reaction and several tests were carried out to validate the reactor features. The results obtained demonstrate that the catalysts activity in the reaction is improved with the application of the novel reactor respect the conventional fixed- and fluidized-bed ones and neither catalyst sintering, nor pressure drop was appreciated during the catalytic tests. At the best reaction conditions, Tecnalia's multichannel minireactor can handle 820 Nm^3/h of CO_2 per square meter of channel section showing the enormous potential of the new reactor concept.

Keywords Sabatier reaction · Microstructured reactor · Continuous-flow chemistry · CO_2 · Natural gas · Heterogeneous catalysis

1 Introduction

Currently, anthropologic CO_2 emissions area of a huge environmental concern. While CO_2 capture and sequestration (CCS) technology is well studied and technologically mature, the CO_2 use as C1 feed-stock as well as its efficient and selective conversion into chemicals and/or fuels is still hampered by mainly by technical issues. In this regard, the Sabatier or methanation reaction [1] for methane production by CO_2 reduction with H_2 in the presence of a heterogeneous, mainly Ru or Ni-based, catalyst (Scheme 1) has gained more interest in the last years due to its application in power-to-gas technology and biogas upgrading [2, 3]. Sabatier reaction usually takes place at temperatures from 200 to 400 °C and pressure from 1 to 30 bar, achieving conversions from 80 to 90% in the presence of supported on alumina (Al_2O_3) Ni or Ru catalysts [4]. It is noteworthy to say that at temperatures above 500 °C the favored reaction is the reverse water gas-shift (RWGS) to produce syngas. However, at low temperatures, the reaction isn't kinetically favorable, so it is necessary the use of a catalyst for carrying out the reaction. Due to its exothermicity, the heat produced during the reaction should be removed continuously to avoid the hot spots and catalyst sintering.

Although Ru-based catalysts are so far, the more active and selective catalysts in the Sabatier reaction and they are active even at low temperatures (< 200 °C), the Ni-based ones, that show good activity and selectivity but at higher temperatures, are widely used mainly due to their lower cost in comparison with Ru-based catalysts. On the other hand, it is well known that the metal dispersion of the support is a key parameter to minimize catalytic sintering, thus support material selection is highly important [5]. In this sense, Al_2O_3 is the most often used support in the preparation of Ni methanation catalysts but also other support materials such as SiO_2, MgO, $MgAl_2O_4$ or $CaAl_2O_4$ are employed by the major catalysts manufacturers namely, The Badische Anilin- und Soda-Fabrik (BASF), Haldor-Topsoe A/S,

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Scheme 1 Ni-catalysed Sabatier reaction

$$CO_2 + 4H_2 \xrightarrow[300\text{-}400\ ^{o}C]{\text{Ni catalyst}} CH_4 + 2H_2O \qquad \Delta H = -167\ KJmol^{-1}$$

Clarian International ltd., Unicat Catalyst Technologies, Inc. and Johnson Matthey.

The Sabatier reaction has been industrially developed by Lurgi, Tremp™, Conoco/BGC, HICOM, Linde, RMP and ICI/Koppers in fixed- or fluidized-bed reactors. Fixed-bed reactors can be operated adiabatic or isothermally with 2–5 reactors in series with internal or external reactor heat exchange to improve thermodynamically the formation of methane. As consequence, the design of the reactor is complex. On the other hand, fluidized bed reactors offer the suspension of the catalytic bed with the reaction gases, which allows a high energy transfer but a poor mass transmission. In addition, catalyst attrition could take place reducing the process efficiency.

Consequently, different types of reactors have appeared during last years to overcome current reactors drawbacks and improve the process efficiency g.e. bubble column or microstructured reactors. The later are discrete units formed by multiple micro- or milli-channels used in process intensification systems, where a catalyst is deposited inside the channels and the reaction gases go through them. Normally, inner diameters are in the range of 10–100 micra and 1–10 mL for microchannel reactors and for millichannels reactors respectively [6]. These kind of reactor have a large surface to volume ratio in comparison with the conventional ones, leading to dramatically improved mass and heat transfer coefficients [7, 8]. This feature minimizes hot spots formation, thus avoiding or minimizing catalysts sintering and increasing the reaction performance 10–20% compared to conventional reactors [9, 10]. Furthermore, the modular nature of this kind of reactors allows the scale up process very easy since it is based on the unit replication and not in the reactor size increase and, consequently, the implementation of a process based in microstructured reactors at industrial level is much faster and flexible to the production needs. The microstructured reactors, due to their intrinsic properties such us its size and kinetic characteristics, have a wide application scope g.e. in production of high purity chemicals, portable plants, microencapsulation, emulsification and synthesis of materials [11, 12].

Here, it is reported the employment of the microstructured reactor concept developed in Tecnalia R&I consisting of 16–388 channels with an internal diameter of 1.75–2 mm in the Sabatier reaction in the range of 200–400 °C and 15–25 bar in the presence of Ni-based catalyst. The performance in terms of efficiency of the designed reactor showed to be superior compared to the traditional fixed-bed reactors. Due to the number of channels and their small internal diameter gas-catalyst contact is improved achieving good mass and energy transfer. Furthermore, the efficient heat removal avoids the formation of hot-spots in the catalyst bed and consequently no catalysts sintering was observed. This new reactor concept showed to be easily scaled-up and at the best reaction conditions, Tecnalia's multichannel minireactor could handle 820 Nm^3/h of CO_2 per square meter of channel section.

2 Experimental Part

2.1 Materials

All manipulations were carried out under normal atmosphere conditions otherwise stated. γ-Al_2O_3 used as support material was purchased from Alfa Aesar (99.97%) with a surface area between 80 and 120 m^2/g and particle size <220 µm. Ni precursor, $Ni(NO_3)_2 6H_2O$ salt, was purchased from Sigma-Aldrich. Hydrogen gas (Alphagaz) and CO_2 gas (99.99%) was purchased from Air Liquide.

2.2 Catalyst Preparation

The Ni-based catalyst on γ-alumina was prepared by impregnation method using the following procedure: The Ni precursor salt ($Ni(NO_3)_2 6H_2O$, 6.2 g) was dissolved in 6 mL of deionized water. Then the desired amount of support material (γ-Al_2O_3, 4gr.) was added and the mixture stirred for 10 min. After, the resulting solid was dried in an oven at 110 °C for 6 h and then milled to homogenize the solid. The obtained powder was calcined in a muffle at 450 °C for 4 h, applying a heating ramp of 2 °C/min from RT. After calcination and prior to be used the catalyst was reduced under Formier gas 650 °C for 2 h with a heating ramp of 2 °C/min from RT.

2.3 Catalyst Characterization

Metal content in the final catalytic system was analyze by means of Plasma Emission Spectrometer ICP/OES Axial. Particle size was determined by sieved mesh.

2.4 Set-up of the Test Rig

To select the best operation/reaction conditions for the Sabatier reaction using a multichannel minireactor, several reaction conditions were tested in the test rig depicted in Fig. 1. The test rig is composed by three mass flows controllers, two condensation systems (one at 5 °C at another one at – 5 °C),

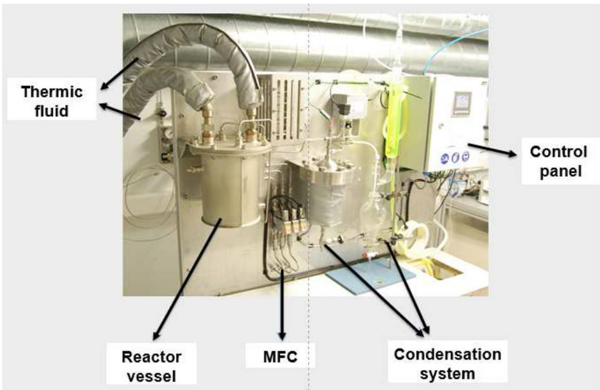


Fig. 1 Test rig at Tecnalia R&I

a reactor heating system filled with a thermal fluid (TOOLTHERM SH-3), a control panel unit and a microGC unit for the continuous analysis of the reaction outlet. With the goal of checking the advantages of the millichannel reactor over the conventional fixed bed both a conventional fixed-bed reactor and a 16 channels minireactor where placed alternatively in the test rig. The main difference between the two reactors is their inner diameter, being the fixed bed of 9 mm and each channel of the minireactor of 1.75 mm. The working temperatures and pressures in the test rig ranged from RT to 900 °C and from atmospheric to 50 bar respectively. To control the temperature of the process in both reactors two thermocouples were placed, one in the thermal fluid vessel and the second one in the gases exit pipeline.

2.5 Catalytic Test in Multichannel Minireactor and Fixed-Bed Reactors

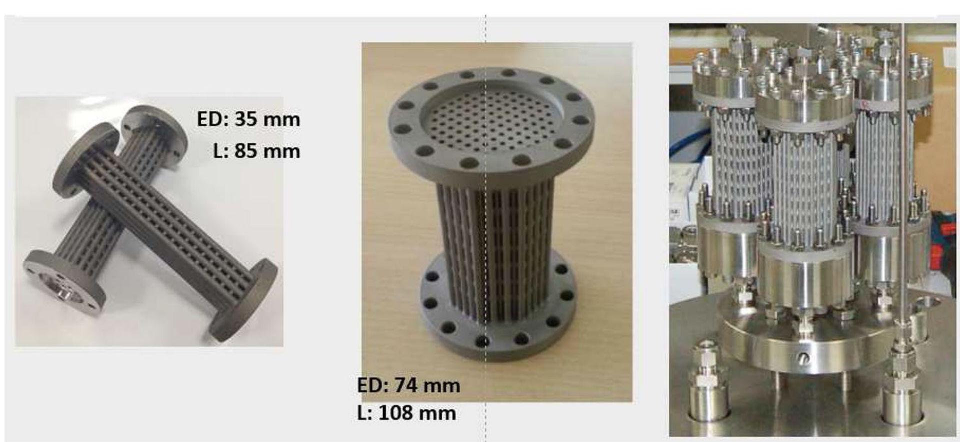
In a typical experiment, 2.5 g of catalyst were placed in a stainless steel multichannel minireactor (16 channels, inner diameter 1.75 mm) or a fixed-bed reactor having an inner diameter of 9 mm. The feed was a CO_2 and H_2 mixture with a constant H_2/CO_2 ratio of 4. The experiments were carried out at different temperatures from 200 to 400 °C at 15 bar and with a constant space velocity of 30,000 h^{-1}. Reaction products were analyzed continuously by Agilent (3000A) micro-gas chromatography with three columns connected to a thermal conductivity detector (TCD).

3 Results and Discussions

3.1 Multichannel Minireactor Design

A new concept of microstructured reactor have been developed and designed by Tecnalia Research and Innovation (R&I) using novel and advanced additive technologies [13]. The use of this novel 3-D printing manufacturing processes has huge advantages over other conventional techniques. In this sense, additive technologies allow to manufacture a reactor in a single part and to have a more precise control during the building up process. Tecnalias' designed multichannel minireactor consists in a bundle of channels with an internal diameter in the order of 1–4 mL as showed in Fig. 2. As consequence of the small inner diameter of the channels, a very high surface area/volume ratio is achieved leading to a dramatic increase of the overall mass and heat transfer and therefore further increase of the overall process productivity. The selected construction material was stainless steel AISI 316L due to its general use and its good corrosion resistance. Each channel is filled up with the needed catalyst. The reaction gas mixture flows through the catalyst placed in the millichannels uniformly due to a specifically designed flow distributor placed before the minireactor inlet. This designed millichannel reactor allows to remove the heat generated in an exothermic reaction, such as the studied one (Sabatier reaction), much easily that in a conventional fixed-bed reactor due to the smaller inner diameter and to the gaps between each millichannel that allows the thermal fluid circulating around them, thus removing the heat generated efficiency.

Fig. 2 Developed multichannel reactor using additive technologies by Tecnalia R&I (16; 68 and 388 millichannel reactors developed)



Thanks to the design of the reactor, the gas–solid contact between reactants and catalyst is increased and the energy transfer is improved. In addition, Tecnalia's designed multichannel minireactor allows the execution of the studied reaction (Sabatier reaction) in only one stage, compared to the traditional several stage processes.

3.2 Catalytic Tests in Sabatier Reaction Multichannel Minireactor Versus Fixed-Bed Reactor

CO_2 catalytic hydrogenation tests with the prepared Ni on alumina (25% Ni) catalyst were performed in the test rig described in the experimental part using as reactors a fixed-bed and the Tecnalia's developed multichannel minireactor. Firstly, the influence of the temperature on the catalytic performance of the prepared Ni-based catalyst in both reactors was studied and the results depicted in Table 1. As can be observed, when a fixed-bed reactor was used the CO_2 conversion increased from 56.6 to 83.4% when the temperature was increased from 200 to 400 °C (entries 1 and 9, Table 1). In the same way, the selectivity to CH_4 increased from 61.3 to 92.2% at 200 °C and 400 °C respectively (entries 2 and 10, Table 1). On the other hand, when the fixed-bed reactor was substituted with the multichannel minireactor both the CO_2 conversion and the selectivity to CH_4 clearly increased at the same reaction temperature. The best performance of the Ni catalyst was achieved in the multichannel minireactor at 350 °C, being the conversion CO_2 and the selectivity to CH_4 91.6% and 100% respectively (entry 8, Table 1).

Table 1 Performance comparison in the Sabatier reaction between fixed-bed reactor and 16 multichannel minireactor technologies

Entry	Reactor type	Temperature (°C)	CO_2 conversion (%)	CH_4 selectivity (%)
1	Fixed-bed[a]	200	56.5	61.3
2	Multichannel minireactor[b]	200	68.8	89.1
3	Fixed-bed[a]	250	65.7	89.7
4	Multichannel minireactor[b]	250	82.3	98.7
5	Fixed-bed[a]	300	75.4	90.0
6	Multichannel minireactor[b]	300	93.5	94.2
7	Fixed-bed[a]	350	81.9	90.1
8	Multichannel minireactor[b]	350	96.1	> 99
9	Fixed-bed[a]	400	83.2	92.2
10	Multichannel minireactor[b]	400	95.9	> 99

Reaction conditions: pressure = 15 bar; GHSV = 30,000 h^{-1}; $H_2/CO = 4$; Ni/γ-Al_2O_3 (25.2% Ni)

[a]9 mm inner diameter

[b]1.75 mm inner diameter, 16 channels

As conclusion from the temperature study for the Sabatier reaction, it can be deducted undoubtedly that the overall performance of the prepared catalysts in the multichannel minireactor is superior compared with the performance in the same conditions in the conventional fixed-bed reactor, as can be seen in Fig. 3.

In addition, the synthetic natural gas (SNG) obtained with the multichannel minireactor at the best reaction conditions fulfil all requirements and specifications of non-conventional gases to be injected into the gas grid in Spain (≥ 95%mol CH_4; ≤ 5%mol H_2; ≤ 2.5%mol CO_2) [12].

3.2.1 Multichannel Minireactor Scaling-up

As mentioned before, one of the main advantages of the microstructured reactors is their modular nature, which allows by simple replication the further scaling-up of the reactor. Therefore, the millichannel reactor developed by Tecnalia can be scaled-up accordingly as depicted in Fig. 4. The simplest unit for its replication is the monochannel (Fig. 4a), which has the right dimensions to host the catalysts and to carry out the reaction in an efficient way. After verifying the monochannel design, the total reactor dimension to build up depends mostly on the required production

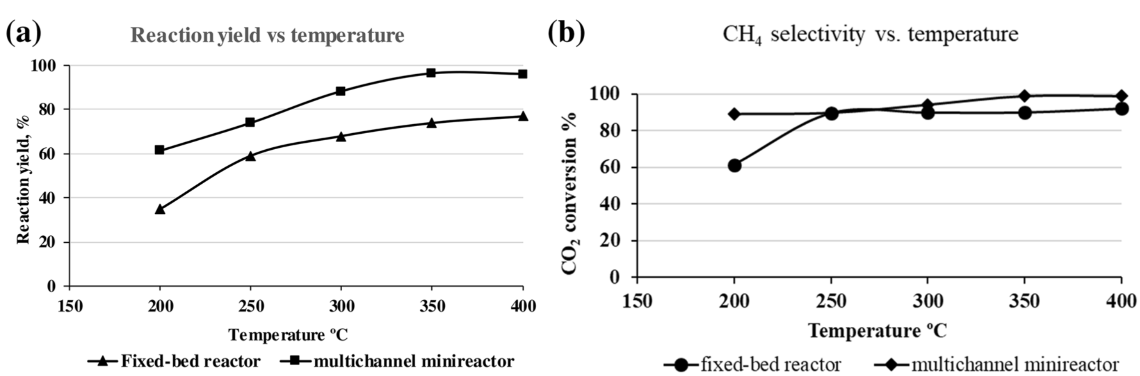


Fig. 3 **a** Reaction yield and **b** CH_4 selectivity versus temperature in fixed-bed and multichannel minireactors

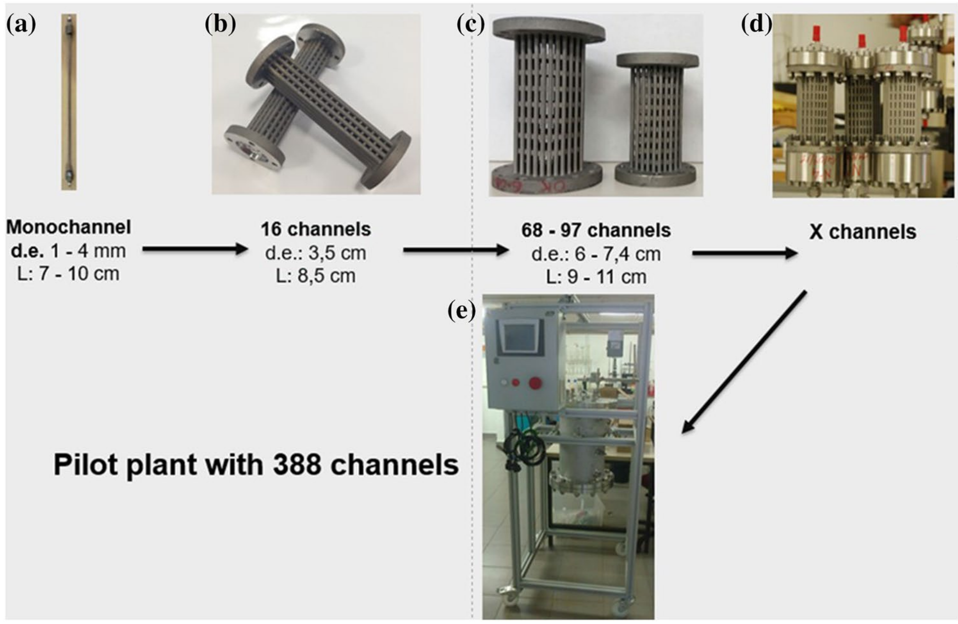


Fig. 4 Multichannel minireactor scaling-up from monochannel to pilot scale

Table 2 Number of channels for different production capacities

Number of channels	Total flow (Nm^3/h)	SNG production (Nm^3/h)
400	2.6	0.5
4000	26	5
8000	52	10

capacity, from a lab scale capacity (Fig. 4b, c) to a pilot scale plant (Fig. 4e).

In the studied case reaction (Sabatier reaction), the basic unit (monochannel) was able to treat 6.5 NL/h of gas for a total CH_4 production of 1.3 NL/h at the optimized reaction conditions (entry 8, Table 1) Considering this production capacity of the basic unit, in Table 2 are showed the number of channels needed for a required industrial production.

In fact, during the RENOVAGAS project (Renovagas project funded by the Spanish Ministry of Economy and Competitiveness—MINECO—with the reference number RTC-2014-2975-3) the multichannel minireactor was scaled-up to 388 millichannels to build up a 15 kW demonstration plant to produce SNG by the Sabatier reaction between biogas and H_2 electrocatalytically produced from renewable energy sources. The multichannel minireactor developed by Tecnalia for this project is showed in Fig. 5. As can be seen, the developed minireactor system consisted in a spring pre-heater gas feed (Fig. 5b) the minireactor module with a total of 388 channels (Fig. 5d) and the thermic fluid vessel (Fig. 5e) for the efficient removal of the heat generated during the reaction.

The designed reactor was integrated in a container with the peripheral systems for the overall process (Fig. 6). The auxiliary system is composed by an alkaline electrolyser for H_2 generation, a compressor for obtaining the reaction pressure, a water condenser, and the system for control and monitoring of the process.

The Renovagas pilot plant was tested with real biogas in a waste water treatment plant in Jerez de la Frontera (Spain), obtaining similar results than the achieved in the laboratory plant.

4 Conclusions

Here, it is reported the application of a novel multichannel minireactor technology developed in Tecnalia R&I composed of several channels with an internal diameter in the range of 1.75–2 mm. This reactor has been tested in the Sabatier reaction at 15 bar and different temperatures from 200 to 400 °C in the presence of Ni based catalyst and its performance compared in same conditions with a conventional fixed-bed reactor. The performance of the multichannel minireactor was proved to be superior to the traditional fixed-bed reactor in terms conversion and selectivity. The best results were obtained at 350 °C with CO_2 conversion of 96.1 and selectivity higher than 99% towards CH_4 due to the small internal diameter of the channels having a better the gas feed/catalyst contact and the improved heat transfer that eliminates the formation of hot spots in the catalyst bed. In addition, at the best reaction conditions Tecnalia's developed multichannel minireactor was validated at TRL5 handling 820 Nm^3/h of CO_2 per square meter of channel

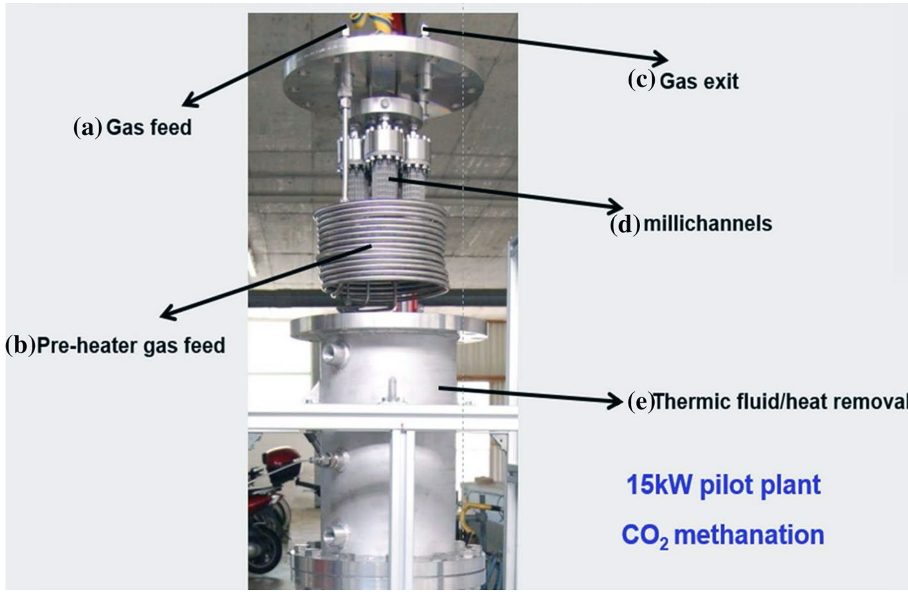


Fig. 5 Multichannel minireactor at Tecnalia R&I

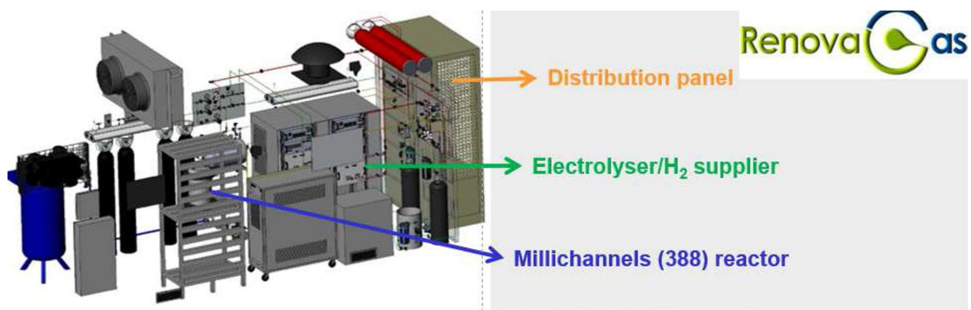


Fig. 6 Renovagas project 15 kW-pilot plant

section. Currently, the new reactor technology developed by Tecnalia is being tested in other reaction of industrial interest.

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